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ANALYTICAL INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: ADVANTAGES, LIMITATIONS, RESEARCH DIRECTIONS AND APPLICATIONS: A LITERATURE REVIEW

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by

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INTRODUCTION

Inductively coupled mass spectrometry (ICPMS) is a recently-developed (first commercially available in 1983) atomic-measurement analytical technique which offers much promise to extend the analytical capabilities of MSL (1).

This is a non-exhaustive review of the literature on ICPMS carried out to provide a technical background in support of a prospectus for its analytical development in the Core Technologies and Services Laboratories of the Mineral Sciences Laboratories.

Despite its short-term general availability, there is already a considerable body of published literature on ICPMS. Indeed, R&D on ICPMS was identified as 16th of the 30 "hottest" fields in science (let alone analytical chemistry) in a 1987 listing by the Institute for Scientific Information (2).

This review covers the analytical advantages and limitations, R&D directions and current fields of applications of ICPMS.

General Principle of Operation

The principle of ICPMS is that an aerosol of the sample is introduced to a high-temperature argon plasma where the sample constituents are completely decomposed and converted to positive ions with high efficiency (e.g. in most cases more than 90%). A small fraction of this plasma (which is at near atmospheric pressure) is passed into a high vacuum mass spectrometer. The spectrometer comprises a tunable mass filter having a resolution of better than one atomic mass unit and an ion-impact photomultiplier counter. The filter is scanned over the mass range of the periodic table, sequentially

passing each isotopic mass of interest in the periodic table (e.g. 1-240 a.m.u.) which is focussed on a detector which records each ion strike. These counts are "binned" in a multichannel scaler and a mass spectrum is built up. The count in each amu unit is proportional to the ion content of the sample.

Being a low-background atomic counting technique of high selectivity, it offers high sensitivity and low detection limits. (e.g. 10^5 to 10^6 counts per second per ppm of ion in the sample solution with backgrounds typically less than 50 counts per second).

The breakthrough advantage of ICPMS is that it permits atmospheric pressure sampling, with high volume sampling, whereas conventional mass spectrometry requires that very small samples be physically inserted into a vacuum chamber and then be pumped down to high vacuum prior to measurement; a process which is time-consuming and fraught with difficulties. The trade off of atmospheric pressure sampling ICPMS is a sacrifice in precision (typically 1-3% RSD with ICPMS), and also a lower mass resolution (e.g. half-peak width greater than about 0.25 a.m.u.) since a more economical quadrupole mass filter is normally used.

ANALYTICAL ADVANTAGES

ICPMS offers the following advantages over alternative atomic measurement techniques available in MSL.

1. Detection Limits:

Reported single element (solution) detection limits for most elements in the periodic table are in the ten to one hundred part per trillion range or comparatively one to four orders of magnitude more sensitive than achievable with ICPAES with the same nebulization system (1,3,4-6) with few exceptions. The ICPMS detection limits approach those achievable with other sensitive atomic analytical techniques - for example neutron activation analysis, atomic fluorescence spectrometry, electrothermal vapourization AAS, - while offering practically-achievable multielement capability (6).

Detection limits for 51 elements in lakewaters based on laboratory and field-carried blanks have been compared, providing interesting comparisons with respect to effects of sampling contamination. The long-term precision information is also instructive and impressive for sub ppb level measurements (4). Detection limits for ICPAES, GFAAS and ICPMS are compared for PGEs in aqueous solutions and ores (22), for 13 elements in aqueous solutions(6). Detection limits, precisions and multielement capability are compared for ICPMS, ICPAES, ICPAFS, GFAAS and FAAS for 32 elements in

aqueous solution (23). Detection limits for rare earth elements by ICPMS, ICPAES, INAA and XRF have been compared(24).

2. Selectivity

Elements from atomic number 3 (lithium) to 238 (uranium) are accessible by ICPMS. Since almost every element has at least one isotope of unique mass, signals are relatively unambiguously assignable to sample constituents*.

Furthermore, resolution of one atomic mass unit is readily achievable, giving rise to small relatively constant backgrounds across the mass range. (An isotope giving rise to 10^6 ion counts per second contributes less than one count per second to the background at the adjacent mass, for example, permitting determinations of trace concentrations of an isotope in the presence of major concentrations of an isotope of adjacent mass.)

In application to multielement determinations in complex samples, these features compare favorably with ICPAES where there is considerable potential for emission line spectral interferences. (For an example of the comparative spectral complexity see reference 6.)

*(However, see limitations below).

3. Broad Range and Rapid Multielement Capability:

Published applications of ICPMS to measurements of about 76 different elements in different geological samples was indicated by 1988 (7), only some five years after the availability of the first commercial ICPMS instrumentation (1).

Applications to SRMs of environmental samples - water, airborne particulate and sewage sludge- (18 to 36 elements, ref. 4, and 49 elements, ref. 5), geological materials (33 elements, ref. 8), illustrate the practicality of single-run multiple element determinations with ICPMS.

4. Isotope measurement capability:

Sixty of the 92 elements of the periodic table exhibit two or more naturally occurring isotopes. ICPMS has the capability to measure isotope ratios.

This capability has been exploited to perform ore genesis studies from isotope ratios, however, the precision attainable in ratio measurements (0.1 to 1%) is regarded as insufficient for most geological radiogenic dating applications with the exception of Re/Os (7 and references therein, 16).

It has been suggested that ICPMS measurements of radioisotopes with half-lives longer than 10^4 to 10^5 years should be determinable more efficiently than with nuclear counting methods if electrothermal vapourization ICPMS is employed (19).

Separated stable isotopes of about 50 elements are commercially available (9). Isotope dilution measurements with conventional mass spectrometry (e.g. thermal ionization or spark source MS) are widely regarded as "definitive" analytical measurements because of the intrinsic cancellation of procedural artifacts, identifiable and estimable remaining interferences, and high precision and sensitivity resulting in high confidence in accuracy (17, 18 and references therein). ICPMS is now also being exploited to obtain accurate trace concentration values, with precisions optimally approaching 0.25% (6,7,10,11). Applications of ID-ICPMS are illustrated by determinations of eleven elements in marine sediments(12), four elements in ocean water CRMs (13,14)), platinum group elements (15), and rare earth elements (7,16) in geological CRMs.

The potential for isotope ratio measurements and the availability of enriched stable isotopes introduces the possibility of stable isotope tracer applications. Studies of the nutritional and biomedical uptake of magnesium, selenium, iron and bromine as well as isotope ratios of lead in blood have been studied by ICPMS (19 and references therein, 20). A feature article in the current edition of Analytical Chemistry illustrates the principals and potential of tracers with mass spectrometry detection in proposed labelling of fly ash particulate with rare earth isotopes to track pollution sources (21).

LIMITATIONS

The complications in quantitative application of ICPMS are summarized as matrix, drift, interferences, memory and background (7, 16, 19). These limitations are outlined in the following.

1. Requirement for dissolution and dilution.

The conventional sample introduction by nebulization of a solution aerosol requires solid sample dissolution. Like most analytical techniques, this introduces the potential for both analyte contamination and/or losses.

An additional requirement for nebulization ICPMS is that dissolved solids not exceed about 0.2% to avoid deposition buildup on the sampling orifice and a resultant unacceptable response drift. An analytical dilution factor of 10^3 has the automatic effect of raising detection limits (in terms of solid sample concentrations) by the same factor. Also, decomposition and storage vessels, dilution solvents and reagents used in the decomposition must have extremely low concentrations of analyte contaminants. "Carried" blanks must be measured for accurate work.

The manufacturer of the CANMET ICPMS however indicates that 1.5-3% brine solutions for example can be aspirated with calibration stability of about 5% (25).

2. Matrix effects

Even at relatively low dissolved solids contents, the slope of calibration curves has been observed to be sensitive to the composition of the solution. The magnitude of this effect is larger than observed for ICPAES, and not completely understood. Acid solutions may be measured, but apparently have a significant concentration-dependent ion suppression effect (minimal in nitric acid solutions). Furthermore, matrix effects have been found to be a function of the ion mass (e.g. more suppression at lighter masses (19). Matrix matching of standards, the use of internal (sensitivity) standards, and standard additions calibrations are strategies used to overcome this effect (e.g. 26).

3. Memory effects

Elements which form refractory oxides (e.g. Al, Ti, Ca, Nb, Zr, Cu ...) tend to build up on the interface sampling cones, later to be released and to contribute to the background (16). Steady-state backgrounds normally exist during run periods, permitting their correction, however a frequent maintenance regime of cone cleaning is required to maintain acceptable background levels. Similarly extended washout periods of the tubing/ nebulizer / torch system may be required to reduce backgrounds of high analyte concentration elements from a previous sample, if the next sample contains low levels of the analyte. Aspiration of 0.2% HF/ 2% HNO3 for two minutes was required to remove thorium memory effects in the analysis of electronic grade quartz for example (27).

4. Response drift

Even with relatively dilute solutions, instrument response drift in relatively short time frames occurs. Analytically, this is compensated by the use of internal drift monitor isotopes, frequent recalibrations, and the use of standard additions calibrations.

5. Molecular ion interferences

Formation of molecular ions arising both from the plasma gas (and impurities therein) and the analytical solution represent potential interferences to trace element determinations in ICPMS.

With nebulized aqueous solutions, unipositive molecular ions corresponding to hydrides, carbides, nitrides, oxides, hydroxides and dimeric species of argon, oxygen, nitrogen are present in the mass spectrum (28)*. This represents a considerable interference potential for a number of analytes up to mass 82, a potential which increases as the concentration level of an analyte isotope decreases.

The problem is exacerbated when percentage levels of hydrochloric, sulphuric or phosphoric acids are present since analagous unipositive species such as SO, SO_2, SO_3, ClO, PO, ArCl, ... are formed (28). For this reason, nitric acid is the dilution acid of choice for ICPMS.

To add to this problem, molecular ions (oxides and hydroxides) are formed appreciably from a number of probable analyte constituents in geological work (29, 30, 31). Oxide to unipositive ion ratios can be minimized by nebulizer flow control, with some sacrifice in unipositive ion sensitivity (29). With "typical" tuning it is suggested that oxides are at most 2% of the parent with the CANMET ICPMS (31). In addition, a number of elements which exhibit relatively low second ionization potentials can give rise to doubly charged ions (29, 31). This results in ICPMS peaks at mass/2, with interference potential at these masses. The highest ratio M^{2+}/M^{+} (Ba) is reportedly of the order 1% with "typical tuning" (31). Additionally, species MH^{+} and MM'^{+}, particularly when M is an alkalai metal, are observed at high concentrations (as in brine, seawater or urine samples, for example).

Analytically, oxide interferences are typically corrected by establishing proportional correlations between the unipositive parent under the tuning conditions used with a surrogate matrix (e.g. 30). Thorium has been applied as an internal oxide/parent ratio-change monitor (8).

*Even high purity argon may contain ppm levels of CO2, hydrocarbons, and nitrogen, and even pure water contains dissolved levels of air and CO2. Unipositive ions of halides, xenon, krypton and mercury have also been seen as ubiquitous contaminants in preliminary runs at CANMET.

RESEARCH AND DEVELOPMENT DIRECTIONS

It is obvious that ICPMS is not a turnkey panacea for all atomic measurement problems. Considerable analytical expertise is still involved in development of successful applications. Examples of the development requirements can be seen in applications to determinations of 33 elements in rock samples (8) and the determination of nickel in urine (32) (both applying physical corrections with no prior matrix separations), and the determinations of elements in seawater (14) and platinum group elements in rocks (15, 33) (applying combinations of chemical preconcentrations, isotope dilution and physical corrections).

Apart from fundamental R&D (studies of ion processes in the plasma and the mass spectrometer), research tends to alternatives to nebulizer sample introduction to improve sensitivity, throughput, and to overcome some of the limitations described above, or the interfacing of chromatographic methods to achieve similar ends and also obtain speciation information.

1. Alternative sample introduction:

The principal limitations of nebulization ICPMS are the high solvent/sample ratio required to minimize cone deposition of refractory elements (raising detection limits and introducing spectral interferences) and the volume of solution consumed in equilibration of the nebulization system and during measurements. There is considerable R&D involving alternative injection to the plasma including filament loop injection (34), slurry nebulization (references in 19), electrothermal vapourizaton (35), direct injection nebulization (36), flow injection (e.g. 25 and references in 19), spark ablation (37) and laser ablation (37-41).*

Laser ablation systems for ICPMS have been available commercially for some time now. The obvious appeal of ablation is the elimination of sample dissolution chemistry. A limitation is calibration of the vapourization process, which is bound to be matrix-dependent, and closely matched standards are apparently required for quantitative work. For this reason, applications to impurities in refractory materials (e.g. zircons, 37), and the measurement of economically important trace impurities in commodities having available CRMs (metals, alloys, pure commercial minerals) are the first probable targets for this technology. However, semi-quantitative results for trace elements in directly-ablated rock standards is encouraging (41). Preparation of heterogeneous samples as glasses or solid solutions (e.g. borate fusion of geological samples, lead fire assay beads) is another path for overcoming calibration problems with ablation.

* R&D applying electrothermal vapourization and solid sampling ICPMS to geological samples is in progress at the GSC (C. Gregoire).

2. Matrix separation/preconcentation and speciation.

The other primary areas of analytical R&D are optimizing the preparative separation chemistry to remove the major (interferant) matrix constituents from - and/or to obtain preconcentrations of- target trace analytes , and the use of ICPMS as a detection system for speciation measurements applying chromatography. Separation development is both in conventional off line "batch" mode, but increasingly by on-line chromatography using flow injection technology.

Silica-immobilized 8-hydroxyquinoline was used in an on-line flow injection system to extract a number of trace metals in tandem from the major alkali and alkaline earth elements in seawater (14). Removal of these same matrix elements was accomplished by bis(carboxymethyl)dithiocarbamate immobilized on a polymer resin using a similar flow-injection system (42). Ion exchange to concentrate trace metals in a flow injection system has been described (refs. in 13, 43, 44). Anion exchange collection of gold cyanide has been used to measure extremely low (fentomolar) concentrations in natural waters using on-line flow injection (45, 46).

A 1990 review of atomic mass spectrometry cites five papers which demonstrated speciation capability (measuring the amount of an element present in a particular ionic or molecular form in a sample) using ICPMS as the detection system for chromatography (arsenic, mercury and tin compounds) (19). The reviewer however comments: "The application of the ICPMS technique as a powerful (but expensive) *multielement* detector for chromatography has yet to be demonstrated by real sample application, however.". Speciation measurements by HPLC/ICPMS are being actively pursued at NRC (14).

The potential for response speciation (here using ion exchange resins with FAAS detection) has also been demonstrated (44). Element forms were differentiated on the basis of their propensity to be retained by anionic and cationic exchange resins.

The application of gas-chromatography/ ICPMS has also been demonstrated (47). Different organics were identified by C:X ratios where X is halogen, N, or O; and C,N and halogen isotope ratios were measured.

AREAS OF APPLICATIONS

References cited above amply demonstrate the broadening range of applications of ICPMS in the eight years since its commercial availability. The applications to date generally take advantage of one or more of the high sensitivity (low detection limits), relative freedom from interferences, rapid broad range of multielement capability, and/or isotope discrimination ability of ICPMS.

1. Environmental Analysis

Water analysis and water environmental analysis is evidently a principal field of application (reviewed to 1989 in reference 48, so far not obtained). Surprisingly, 1991 fundamental reviews of environmental and water analysis cite few references to ICPMS applications, and under the headings of municipal and industrial wastewater, no specific ICPMS references appear (49, 50). The capability, however, is amply demonstrated in reference (5).

2. Geological Analysis

ICPMS has played a principal role in geological analysis since its availability. This is largely due to its sensitivity (applicable to geochemical exploration and the importance of trace element ratios and isotope ratios in defining mineralogical history). Determinations of rare earth elements (e.g. 7, 16, 24, 51, 52) and platinum group elements (e.g. 7, 15, 18, 33, 22, 52, 53) have featured prominently in this area. Recent applications to geological materials are reviewed in refs. 15 and 37.

Application of ICPMS for certification measurements of trace elements in geological (rocks, soils) and environmental (fresh and sea waters, sediments, animal tissues) is becoming prominent.

3. Biological Analysis

Application of ICPMS is prominent in biological studies particularly from the viewpoints of measurement of toxic elements in tissues and fluids, isotopic distribution in uptake, and tracer applications (15).

4. Metallurgy & Materials

Published applications in metallurgy and materials analysis to 1990 are reviewed in reference 15. These tend to be of trace elements subject to specification limits in high purity materials such as gold, steels and alloys, alloys for the nuclear industry and frequently involve some separation pre-chemistry. It is expected that development of laser ablation sampling will play a major role in the analysis of these types of materials in the future.

CONCLUSION

Published applications of ICPMS in mining and metallurgical processing studies are evidently rare, although a thorough search has not been completed. (This likely stems from both proprietary applications remaining unpublished and ICPMS technology being available to a restricted number of larger industrial facilities at present). The obvious advantages can be inferred from the geological, metallurgical, environmental (and even biological) references cited above.

Knowledge of low concentrations of elemental concentrations in process solutions, waste streams, intermediates and products can be applied valuably to further the knowledge of metallurgical processes. Availability of ICPMS at CANMET should extend these capabilities. Coupling of ICPMS to sophisticated analytical separation technologies such as HPLC offers further potential to provide speciation information of trace constituents. Isotope measurement capability may be exploited to delineate the fate of process or waste constituents.

As this is new analytical technology for CTSL, MSL staff, there is an initial threshold of initial experience which must be overcome to become familiar with the instrumentation and its capabilities and limitations. This can be accomplished by application to relevant geological and solution reference materials. It is expected that this demonstration period can be accomplished in relatively short order, whereupon service applications for elemental determinations can proceed and more sophisticated service capabilities can be developed.

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